

Hierarchical self-assembly of the DNA-grafted supramolecular polymers

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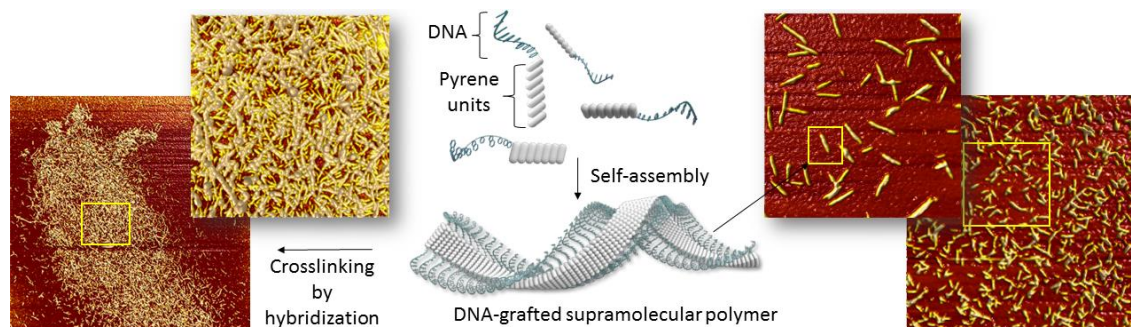
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Conjugation of functional entities with a specific set of optical, mechanical or biological properties to DNA strands allows engineering of sophisticated DNA-containing architectures. ^[1] Among various hybrid systems, DNA-grafted polymers occupy an important place in modern materials science. ^[3] In this contribution we present the non-covalent synthesis and properties of DNA-grafted linear supramolecular polymers (SPs), which are assembled in a controllable manner from short chimeric DNA-pyrene oligomers. The synthetic oligomers consist of two parts: a 10 nucleotides long DNA chain and a covalently attached segment of variable number of phosphodiester-linked pyrenes. The temperature-dependent formation of DNA-grafted SPs is described by a nucleation-elongation mechanism.

The high tendency of pyrenes to aggregate in water, leads to the rapid formation of SPs. The core of the assemblies consists of stacked pyrenes. They form a 1D platform, to which the DNA chains are attached. Combined spectroscopic and microscopic studies reveal that the major driving forces of the polymerization are π -stacking of pyrenes and hydrophobic interactions, and DNA pairing contributes to a lesser extent. ^[4] AFM and TEM experiments demonstrate that the 1D SPs appear as elongated ribbons with a length of several hundred nanometers. They exhibit an apparent helical structure with a pitch-to-pitch distance of 50 ± 15 nm.

Since DNA pairing is a highly selective process, the ongoing studies are aimed to utilize DNA-grafted SPs for the programmable arrangement of functional entities. For example, the addition of non-modified complementary DNA strands to the DNA-grafted SPs leads to the cooperative formation of higher-order assemblies. Also, our experiments suggest that the fluorescent pyrene core of 1D ribbons serves as an efficient donor platform for energy transfer applications.



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References

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